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Inductive Effect of Polar Substituents on Carbon-Hydrogen Stretching Vibrations of Aliphatic Hydrocarbons*

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Infrared absorption studies have been made of the carbon-hydrogen stretching frequencies as observed with a lithium fluoride prism for homologous series of aliphatic alcohols, fatty acids, alkyl bromides and hydrocarbons. It was pointed out in all series of compounds except hydrocarbons, that the methyl stretching frequency, ν , decreases with the length of the carbon chain, n , *i. e.* the distance between the methyl group and the polar substituent in a molecule. Except the lowest member of each series, the frequency shift was expressed as

$$\nu - \nu^0 = Ae^{-Bn}$$

where ν^0 is the methyl frequency of saturated hydrocarbon molecules, which remains constant for all members of this series. A and B are the experimental constants.

This equation was also derived theoretically, the frequency shifts being ascribed to the inductive effects of the polar substituents transmitted through the carbon chain, and physical meanings of constants A and B were discussed. A is a constant characteristic of the polar groups, and the constant B relates only to the ratio of the induced charges of two adjacent carbon atoms in the alkyl chain and depends upon the configuration of carbon chain rather than the sort of the polar substituents.

INTRODUCTION

According to the principle of independent surface action of molecule proposed by Langmuir,¹⁾ the field of force about any particular group or radical in a large organic molecule is characteristic of that group and, as a first approximation, is independent of the nature of the rest of the molecule. This principle was based on the fact that the total surface energy of liquid normal alcohols or fatty acids takes almost the same value as that of saturated hydrocarbons. Indeed, it is true for alcohols and acids longer than eight-carbon chain. However, it is known that the surface energy of shorter carbon chain compounds considerably depends upon their chain lengths²⁾.

Palit³⁾ discussed the relation between solubilities of polar alkyl compounds, such as, alcohols, acids, ketones and aldehydes and their chain lengths, and pointed out that the nearer the average distance between the methyl and the polar groups the more the compounds are soluble. He ascribed the increase in the solubilities of the compounds to the induced polarity of the C-H bonds, as a result of which hydrogen atoms near the polar group can participate in the hydrogen bond-forma-

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tion. However, no confirmation of this suggestion has been shown yet.

Sheppard,⁴⁾ Bellamy and Williams⁵⁾ and Wilmshurst⁶⁾ investigated infrared spectroscopically the inductive effect of polar substituents on various modes of the CH_3 vibration of methyl compounds and discussed the relation to electronegativity of the substituents. Pozefsky and Coggeshall⁷⁾ measured the C-H stretching frequencies of sulfur-containing compounds and oxygenated materials, and discussed qualitatively the effect of the introduction of sulfur or oxygen atoms into the molecule. Further we can find a number of infrared absorption studies⁸⁾ concerning the inductive effect, but there are few in which the relationship of the inductive effect to the carbon chain length of the compounds has been discussed.

Present authors intended to confirm infrared spectroscopically the inductive effect of polar substituents on the C-H stretching vibrations of aliphatic hydrocarbons and to examine the relationship to their carbon chain lengths and electronegativity of the substituents.

EXPERIMENTAL

A Perkin-Elmer Model 21 infrared spectrophotometer equipped with a lithium fluoride prism was used. For the wavelength calibration the rotation vibration spectra of methane⁹⁾ at $3170\sim 2880\text{ cm}^{-1}$ region and the C-H stretching vibration bands of polystyrene film¹⁰⁾ were used. The wavelength accuracy in this case was $\pm 1\text{ cm}^{-1}$.

Most of the samples were obtained by careful purification from commercial chemicals of highest purity. 3-Methyl-2-butanol and 4-methyl-2-pentanol were supplied by Dr. H. H. Zeiss of Yale University and used as received. 3-Methyl-3-pentanol and 2-methyl-3-ethyl-2-pentanol were prepared by Professor S. Kunichika of this Institute.

All the samples were measured as solutions appropriately diluted in carbon tetrachloride. A 0.12 mm fixed thickness cell was used, although in several instances a 10.2 mm cell was employed in an attempt to minimize interaction effects by studying dilute solutions.

RESULTS

Tables 1, 2 and 3 show the frequencies of the absorption bands observed in $3000\sim 2850\text{ cm}^{-1}$ region for aliphatic alcohols, fatty acids and alkyl bromides respectively. In Table 4 the frequencies observed for straight-chain hydrocarbons are also shown for reference.

According to the results of Fox and Martin¹¹⁾ and Pozefsky and Coggeshall,⁷⁾ it is reasonable to classify the absorption bands into four groups and to assign as follows:

Band of 2960 cm^{-1} region: The asymmetrical (degenerate) methyl stretching vibration.

Band of 2930 cm^{-1} region: The overlapping band of the asymmetrical methylene stretching vibration and the other characteristic of the methyl group. When the ratio of CH_2 to CH_3 groups is approximately 5 to 1, contribution of the methylene

groups to this band is appreciable. The frequencies of such bands are written in boldface in Tables. Otherwise, an absorption band in this region cannot be positively identified as due solely to a methyl or methylene group.

Table 1. Carbon-hydrogen stretching frequencies for aliphatic alcohols in carbon tetrachloride. (cm^{-1})

	<i>n</i>	2960 cm^{-1}	2930 cm^{-1}	2880 cm^{-1}	2860 cm^{-1}
Straight-chain alcohols					
Methanol	1	<i>a</i> ~2984(w) ^b	2948(s)~2916(w)		
Ethanol	2	2080(s)	~2931(w, b) ^c	~2891(m, b)	
1-Propanol	3	2969(s)	2941(m)	2881(m)	
1-Butanol	4	2963(s)	2937(s)	2876(m)	
1-Pentanol	5	2961(s)	2934(s)	2874(m)	~2866(w)
1-Hexanol	6	2960(m)	2934(s) ^d	2873(w)	2861(m)
1-Heptanol	7	2959(m)	2933(s)	2873(w)	2858(m)
1-Octanol	8	2959(w)	2929(s)	2873(w)	2857(s)
1-Decanol	10	2959(w)	2928(s)	2873(w)	2856(s)
1-Dodecanol	12	2959(w)	2928(s)	~2873(w)	2856(s)
Branched-chain alcohols					
2-Propanol (2) ^e	2	2977(s)	2935(m)	2886(m)	
2-Methyl-2-propanol (3)	2	2976(s)	2937(w)~2910(w)	2877(w)	
2-Butanol (2)	2.5	2975(s)	2934(m)	2881(m)	
3-Methyl-2-butanol (3)	2.67	2969(s)	2935(w)	2883(m)	
3-Methyl-3-pentanol (3)	2.67	2969(s)	~2936(m, b)	2883(m)	
2-Methyl-1-propanol (2)	3	2966(s)	2935(w)	2877(m)	
2-Methyl-3-ethyl- 2-pentanol (4)	3	2966(s)	2939(m)	2877(m)	
4-Methyl-2-pentanol (3)	3.33	2964(s)	2929(w)	2873(m)	
3-Methyl-1-butanol (2)	4	2962(s)	2936(m)	2875(m)	

^a~indicates band positions are approximate. ^b Symbols (s), (m) and (w) indicate band intensities are strong, medium and weak, respectively. ^c Symbol (b) shows bands are broad. ^d Boldfaced letters refer to bands arising mainly from methylene groups. ^e Symbols (2), (3) and (4) after the names of branched-chain alcohols indicate the number of branch is two, three and four.

Table 2. Carbon-hydrogen stretching frequencies for straight-chain fatty acids in carbon tetrachloride (cm^{-1})

	<i>n</i>	2960 cm^{-1}	2930 cm^{-1}	2880 cm^{-1}	2860 cm^{-1}
Methanecarboxylic acid	1	~2986(w, b)	~2926(m, b)		
Ethancarboxylic acid	2	2986(s)	2946(m)~2929(w, b)	~2889(w, b)	
Propane-1-carboxylic acid	3	2970(s)	2937(m)	2879(m)	
Butane-1-carboxylic acid	4	2964(s)	2935(m)	2876(m)	
Pentane-1-carboxylic acid	5	2961(s)	2933(s)	2874(m)	2862(w)
Hexane-1-carboxylic acid	6	2960(s)	2931(s)	2874(w)	2861(m)
Heptane-1-carboxylic acid	7	2959(m)	2930(s)	2873(w)	2859(m)
Octane-1-carboxylic acid	8	2959(m)	2929(s)	~2873(w)	2858(s)
Nonane-1-carboxylic acid	9	2959(m)	2929(s)	~2873(w)	2858(s)

Symbols as in Table 1.

Inductive Effect on Carbon-Hydrogen Stretching Vibration

Table 3. Carbon-hydrogen stretching frequencies for straight-chain alkyl bromides in carbon tetrachloride. (cm^{-1})

	<i>n</i>	2960 cm^{-1}	2930 cm^{-1}	2880 cm^{-1}	2860 cm^{-1}
Bromomethane	1	3047(w)		2960(s)	
Bromoethane	2	2977(s)	2927(s)	2892(w) 2870(s)	
1-Bromopropane	3	2970(s)	2941(m)	2881(m)	
1-Bromobutane	4	2964(s)	2937(m)	2876(m)	
1-Bromopentane	5	2961(s)	2935(s)	2874(m)	2865(w)
1-Bromohexane	6	2960(s)	2933(s)	2873(w)	2860(m)
1-Bromoheptane	7	2959(m)	2931(s)	2873(w)	2858(s)
1-Bromooctane	8	2959(m)	2929(s)	2873(w)	2858(s)
1-Bromodecane	10	2959(w)	2928(s)	~2873(w)	2856(s)
1-Bromododecane	12	2959(w)	2928(s)	~2873(w)	2856(s)

Symbols as in Table 1.

Table 4. Carbon-hydrogen stretching frequencies for straight-chain hydrocarbons in carbon tetrachloride. (cm^{-1})

	2960 cm^{-1}	2930 cm^{-1}	2880 cm^{-1}	2860 cm^{-1}
Propane	2959(s)	2932(m)	2899(m) 2874(s)	
Butane	2958(s)	~2929(m, b)	2874(m)	~2860(w)
Pentane	2960(s)	2929(m)	2874(m)	2860(w)
Hexane	2959(s)	2930(s)	2873(m)	2860(m)
Octane	2960(s)	2928(s)	2874(m)	2856(s)
Dodecane	2959(m)	2928(s)	2873(w)	2855(s)
Tetradecane	2959(m)	2929(s)	2873(w)	2855(s)

Symbols as in Table 1.

Band of 2880 cm^{-1} region: The symmetrical methyl stretching vibration.

Band of 2860 cm^{-1} region: The symmetrical methylene stretching vibration. The bands in this region were observed only when the ratio of CH_2 to CH_3 groups of alcohols, acids and alkyl bromides exceeds 4 to 1, and that of hydrocarbons exceeds 1 to 1.

In Tables 1, 2 and 3, it can be pointed out that for alcohols, acids and alkyl bromides, the bands assigned as due to one of the asymmetrical and symmetrical stretching vibrations of methyl and methylene groups depend regularly upon their chain length. Those absorption bands shift to lower frequency with the increase of the carbon chain lengths of the molecules, approaching the constant values characteristic of each group. However, the symmetrical methyl stretching vibration (2880 cm^{-1} region) of three- or more-branched-chain alcohols shows departure from these tendencies.

On the other hand, the absorption frequencies of each group of hydrocarbon molecules are almost independent of their chain length and show the constant values, which agree well with the frequencies obtained for the longer chain compounds of alcohols, acids and alkyl bromides. Therefore, it may be reasonable to ascribe the frequency shifts observed for three series of compounds to the effects of polar groups in those molecules.

Figure 1 shows the relation between the asymmetrical methyl stretching frequency, ν , and the alkyl chain length, n , for each of the homologous series examined. The quantity n is the measure of the distance between the methyl and the polar groups in a molecule, and for straight-chain molecules it means the carbon number of alkyl chain. Since there are two or more methyl groups in a branched-chain molecule, the average of values calculated for each methyl group in the same way as for straight-chain ones may serve as n in this case. These values are also listed in Tables 1, 2 and 3.

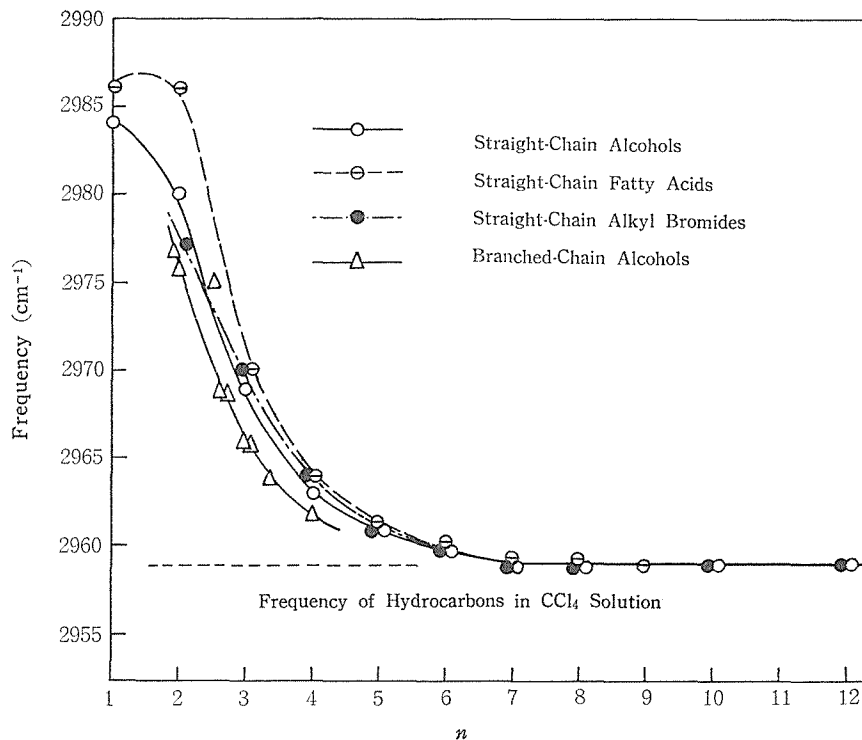


Fig. 1. Plot of asymmetrical methyl stretching frequency vs. carbon chain length n .

In each series of straight-chain compounds, it is found that the frequencies ν decrease exponentially with the increase of their chain length and at $n=6\sim7$ attain a constant value $\nu^0=2959\text{ cm}^{-1}$ which agrees with the frequency of saturated hydrocarbon molecules.

In branched-chain alcohols the frequencies decrease with the chain length in the same way as in the case of straight-chain compounds,* approaching the constant value 2959 cm^{-1} . However, the fact that a curve for branched-chain alcohols lies below that of straight-chain ones, shows the effect of hydroxyl group upon the methyl groups of the former is smaller than that upon the methyl group of the latter of the same n value.

The symmetrical methyl stretching frequencies of alcohols, acids and alkyl bromides also vary similarly to the above with respect to the chain length and

* Only 2-butanol shows departure from these tendencies.

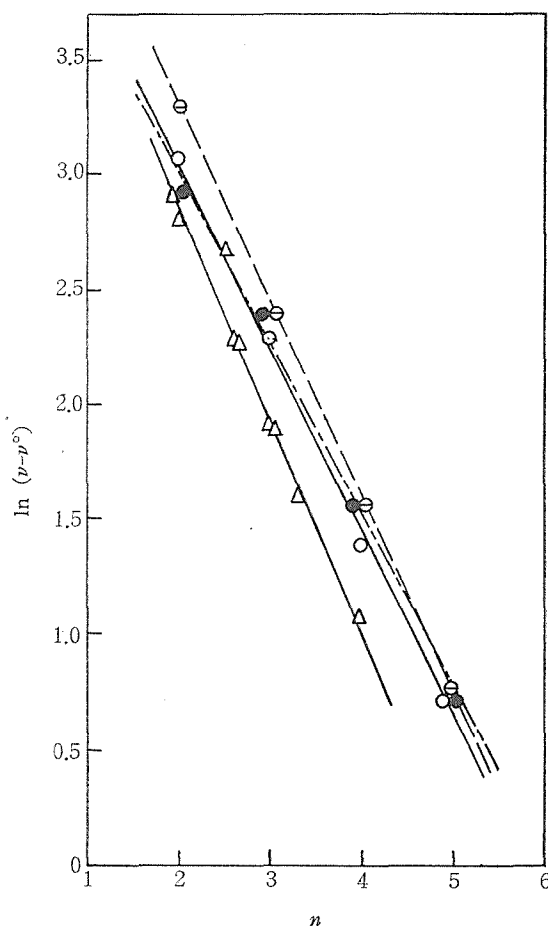


Fig. 2. Plot of $\ln(\nu - \nu^0)$ for asymmetrical methyl stretching vibration vs. carbon chain length n .

$\nu^0 = 2959 \text{ cm}^{-1}$.

Symbols as in Fig. 1.

attain the frequency of hydrocarbon molecule $\nu^0 = 2873 \text{ cm}^{-1}$ at $n = 6 \sim 7$.

Except the lowest member of each series (CH_3X type molecules), plot of $\ln(\nu - \nu^0)$ against n gives the linear relation as seen in Figs. 2 and 3 for the asymmetrical and the symmetrical methyl stretching vibrations, respectively. Therefore, we have a relation

$$\nu - \nu^0 = Ae^{-Bn} \quad (n > 1) \quad (1)$$

where A and B are the experimental constants, values of which are determined for each series of compounds and are shown in Table 5.

THEORETICAL

In this section, the relations between the frequency ν and the chain length n are discussed theoretically on the basis of Pauling's theory¹²⁾ of electronegativity under the assumption that the frequency shifts shown by equation 1 arise from the

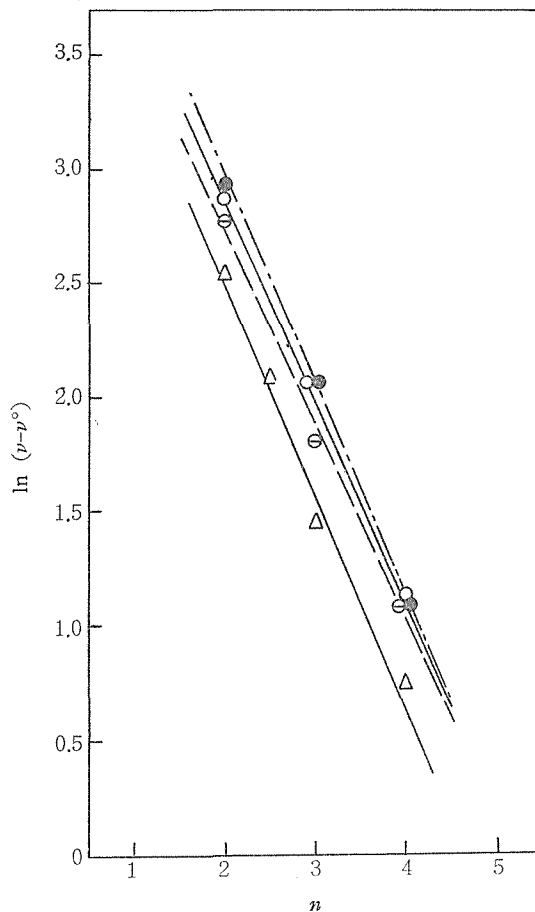


Fig. 3. Plot of $\ln(\nu-\nu^0)$ for symmetrical methyl stretching vibration vs. carbon chain length n .
 $\nu^0 = 2873\text{cm}^{-1}$.

Symbols as in Fig. 1.

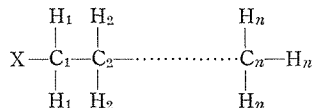
Only the values of two-branched-chain alcohols are adopted for series of branched-chain alcohols (see text).

Table 5. Empirical values of constants A and B for each homologous series.

	Asymmetrical Stretching Vibration $\nu^0 = 2959\text{cm}^{-1}$		Symmetrical Stretching Vibration $\nu^0 = 2873\text{cm}^{-1}$	
	A	B	A	B
Straight-chain alcohol	104	0.80	89	0.81
Straight-chain fatty acid	137	0.83	77	0.78
Straight-chain alkyl bromide	91	0.75	97	0.83
Branched-chain alcohol	107	0.90	82	0.95

inductive effect of the polar groups.

In a mono-substituted straight-chain hydrocarbon molecule



the electrons of carbon and hydrogen atoms may be attracted by an electronegative substituent X, and those atoms may be charged positively in consequence. If the induced charge of a carbon atom C_i adjacent to X is $\delta_{e1}(x)$ in electron units, by Pauling's theory^{12a)}, the increment of electronegativity of C_1 atom, $\alpha(x)$, may be given by

$$\alpha(x) = \frac{s}{1-s} \Delta x_o \cdot \delta_{e1}(x) \quad (2)$$

where s is the screening constant of one valence electron for another in carbon atom, and Δx_o is the electronegativity difference between carbon atom and next atom to the right in the periodic table, *i. e.* nitrogen atom.

According to Ri¹³⁾, the decreasing ratio, σ , of the induced charge on a carbon atom to that of the adjacent one in alkyl chain may be assumed to take a constant value 0.45 throughout a carbon chain. Assuming that the same ratio can be held approximately for the C-H bond,* the increments of electronegativities of C_n and H_n atoms in the methyl group may be given by $\alpha\sigma^{n-1}$ and $\alpha\sigma^n$ ** respectively, because the positive charges on C_n and H_n atoms are $\delta_{e1}\sigma^{n-1}$ and $\delta_{e1}\sigma^n$. Therefore, electronegativities x_{C_n} for C_n atom and x_{H_n} for H_n are written as follows:

$$\left. \begin{array}{l} x_{\text{C}_n} = x_{\text{C}}^o + \alpha\sigma^{n-1} \\ x_{\text{H}_n} = x_{\text{H}}^o + \alpha\sigma^n \end{array} \right\} \quad (3)$$

where x_{C}^o and x_{H}^o are electronegativities for neutral carbon and hydrogen atoms.

The C-H bond length, r_{CH}^o , of hydrocarbon molecules can be expressed by Schomaker and Stevenson's relation¹⁴⁾

$$r_{\text{CH}}^o = r_{\text{C}}^o + r_{\text{H}}^o - \beta(x_{\text{C}}^o - x_{\text{H}}^o) \quad (4)$$

where r_{C}^o and r_{H}^o are the covalent radii for neutral carbon and hydrogen atoms and β is a constant having a value 0.09. Hence, the $\text{C}_n\text{-H}_n$ bond length $r_{\text{C}_n\text{H}_n}$ of the methyl group with induced charge can be expressed as

$$r_{\text{C}_n\text{H}_n} = r_{\text{C}}^o + r_{\text{H}}^o - \beta(x_{\text{C}_n} - x_{\text{H}_n}) = r_{\text{CH}}^o - \alpha\beta(1-\sigma)\sigma^{n-1} \quad (5)$$

According to Gordy,¹⁵⁾ the bond-stretching force constant k of the $\text{C}_n\text{-H}_n$ bond can be related with electronegativities and bond length as follows:

$$k = aN \left\{ \frac{x_{\text{C}_n} x_{\text{H}_n}}{(r_{\text{C}_n\text{H}_n})^2} \right\}^{\frac{3}{4}} + b \quad (6)$$

where N is the bond order, and a and b are the constants which have the values 1.67 and 0.30 when k is measured in $\text{md}/\text{\AA}$, and $r_{\text{C}_n\text{H}_n}$ in \AA units. Neglecting the higher terms of α and σ with respect to n , from equations 3 and 5

* Validity of this assumption is theoretically recognized in first approximation¹³⁾.

** For simplicity, the symbol (X) in $\alpha(X)$ and $\delta_{e1}(X)$ is neglected. Here, it is assumed that α value of H_n atom is the same as that of C_n atom.

we have

$$x_{C_n}x_{H_n} = x_{C^0}x_{H^0} + X\sigma^{n-1} \quad (7)$$

where

$$X = \alpha(x_{H^0} + \sigma x_{C^0}) \quad (8)$$

and

$$(r_{C_nH_n})^2 = (r_{CH^0})^2 - Y\sigma^{n-1} \quad (9)$$

where

$$Y = 2\alpha\beta r_{CH^0}(1 - \sigma) \quad (10)$$

Substitution of equations 7 and 9 into equation 6 and neglect of the constant b lead to the equation

$$k = aN \left\{ \frac{x_{C^0}x_{H^0}}{(r_{CH^0})^2} \frac{1 + \frac{X}{x_{C^0}x_{H^0}}\sigma^{n-1}}{1 - \frac{Y}{(r_{CH^0})^2}\sigma^{n-1}} \right\}^{\frac{3}{4}} \quad (11)$$

By taking

$$k^0 = aN \left\{ \frac{x_{C^0}x_{H^0}}{(r_{CH^0})^2} \right\}^{\frac{3}{4}} \quad (12)$$

as the force constant of the C-H bond without induced charge, equation 11 becomes approximately

$$k = k^0 \left[1 + \frac{3}{4} \left\{ \frac{X}{x_{C^0}x_{H^0}} + \frac{Y}{(r_{CH^0})^2} \right\} \sigma^{n-1} \right]$$

Using the known relation

$$\frac{\nu}{\nu^0} = \left(\frac{k}{k^0} \right)^{\frac{1}{2}}$$

and equations 8 and 10, we have

$$\nu - \nu^0 = \frac{3}{8} \frac{\nu^0 \alpha}{\sigma} \left\{ \frac{x_{H^0} + \sigma x_{C^0}}{x_{C^0}x_{H^0}} + \frac{2\beta(1 - \sigma)}{r_{CH^0}} \right\} \sigma^n \quad (13)$$

Here ν^0 is the asymmetrical or the symmetrical stretching frequency of the neutral methyl group and can be written¹⁶⁾ as

$$\nu_{\text{asym}}^0 = \frac{1}{2\pi c} \left\{ k^0 \left(\frac{1}{m_H} + \frac{3}{2m_C} \sin^2 \phi \right) \right\}^{\frac{1}{2}} \quad (14)$$

for the asymmetrical stretching vibration, and

$$\nu_{\text{sym}}^0 = \frac{1}{2\pi c} \left\{ k^0 \left(\frac{1}{m_H} + \frac{3}{m_C} \cos^2 \phi \right) \right\}^{\frac{1}{2}} \quad (15)$$

for the symmetrical stretching one, where c is the light velocity, ϕ the angle between the C-H bonds and the symmetry axis of the methyl group, and m_C and m_H are the masses of carbon and hydrogen atoms respectively.

From the derivation of equation 13, it is readily seen that the first term in the right side of this equation gives the contribution of the increment of electronegativity for C_n and H_n atoms and the second term gives the contribution of decrement of the C_n-H_n bond lengths.

If we take

$$A = \frac{3}{8} \frac{\nu^0 \alpha}{\sigma} \left\{ \frac{x_H^0 + \sigma x_C^0}{x_C^0 x_H^0} + \frac{2\beta(1-\sigma)}{r_{CH}^0} \right\} \quad (16)$$

and

$$B = -\ln \sigma \quad (17)$$

equation 13 can be reduced to a simple form

$$\nu - \nu^0 = Ae^{-Bn}$$

which is the same type as the empirical relation 1 obtained for the asymmetrical and the symmetrical methyl stretching frequencies of homologous series of alcohols, acids and alkyl bromides. From equations 16 and 17, it is evident that A is a constant which depends upon α , hence, A is characteristic of the polar groups, and B relates only to σ and is independent of the sort of the polar substituents.

Now, substituting the numerical values $r_C^0 = 0.77 \text{ \AA}^{14)}$, $r_H^0 = 0.37 \text{ \AA}^{14)}$, $x_C^0 = 2.5^{12)}$ and $x_H^0 = 2.1^{12)}$ into equation 4, we have $r_{CH}^0 = 1.10 \text{ \AA}$. In equation 12, use of these values and $N=1.0$ leads to the result

$$k^0 = 5.0 \text{ md/\AA}$$

Then, if we take $m_H = 1.0$, $m_C = 12.0$ and $\phi = 70^\circ 32'$ assuming the tetrahedral angle for the methyl group, the stretching frequencies of neutral methyl groups are obtained as

$$\nu_{\text{asym}}^0 = 3070 \text{ cm}^{-1} \text{ and } \nu_{\text{sym}}^0 = 2950 \text{ cm}^{-1}$$

from equations 14 and 15 respectively.

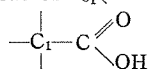
On the other hand, using $s = 0.35^{17)}$ and $\Delta x_0 = 0.5^{12)}$ and assuming

$$\delta_{c_1}(\text{OH}) = 0.13^{18)}, \delta_{c_1}(\text{COOH}) = 0.24^* \text{ and } \delta_{c_1}(\text{Br}) = 0.19^{18)}$$

Table 6. Comparison between theoretical and empirical values of various constants in a relation $\nu - \nu^0 = A \exp(-Bn)$.

	Asymmetrical Stretching Vibration				Symmetrical Stretching Vibration			
	Theoretical		Empirical		Theoretical		Empirical	
	$\nu^0 = 3070 \text{ cm}^{-1}$		$\nu^0 = 2959 \text{ cm}^{-1}$		$\nu^0 = 2950 \text{ cm}^{-1}$		$\nu^0 = 2873 \text{ cm}^{-1}$	
	A	B	A	B	A	B	A	B
Straight-chain alcohol	63	0.80	104	0.80	61	0.80	89	0.81
Straight-chain fatty acid	117	0.80	137	0.83	112	0.80	77	0.78
Straight-chain alkyl bromide	92	0.80	91	0.75	89	0.80	97	0.83
Branched-chain alcohol	63	0.80	107	0.90	61	0.80	82	0.95
	($\sigma = 0.45$)				($\sigma = 0.45$)			
	80	0.92			77	0.92		
	($\sigma = 0.40$)				($\sigma = 0.40$)			

* The value of $\delta_{c_1}(\text{COOH})$ for the structure



is obtained as follows. The induced charges on the C atom in the carboxylic group is calculated as the sum of both contributions from $\text{C}=\text{O}$ and $\text{C}-\text{OH}$ bonds,¹⁸⁾ and the value obtained is multiplied by $\sigma = 0.45$

from equation 2 we have

$$\alpha(\text{OH})=0.035, \alpha(\text{COOH})=0.065 \text{ and } \alpha(\text{Br})=0.051$$

By substitution of these values and 0.45 for σ into equations 16 and 17, we can calculate the numerical values of the constants A and B for each series of compounds. As is shown in Table 6 except the last two rows, the calculated values for A , B and ν^0 are in fairly good agreement with the values obtained experimentally for three homologous series of straight-chain compounds.

DISCUSSION

Inductive Effect on Methyl and Methylene Groups

From the good agreement between the empirical and the theoretical results, it may be concluded that the frequency shifts of the methyl stretching vibrations of alcohols, acids and alkyl bromides are attributed to the inductive effect of the polar groups. That is, the polar group in such a molecule attracts the electrons of the methyl group through the C-C bonds, and in consequence the force constant and the stretching frequencies of the methyl group are increased. This effect decreases exponentially with the increase of the carbon chain length, n , and almost disappear at $n=6$ or more, where the methyl stretching vibrations are independent of the polar group; thus the principle of independent surface action of molecules proposed by Langmuir¹³ holds well.

For the methylene stretching vibrations the same type of frequency shift may be expected to exist as for the methyl stretching vibrations, and the frequencies of every methylene group in a longer chain molecule would decrease with the increase of the distance from the polar group. Therefore the asymmetrical and the symmetrical methylene absorption bands shown in Tables 1, 2 and 3 (the absorptions written in boldface at 2930 cm^{-1} region and the absorptions at 2860 cm^{-1} region, respectively) give the average values of such vibration frequencies of the methylene groups in a molecule. These bands shift towards those of the saturated hydrocarbons with the increase of the carbon chain length as is expected.

The fact mentioned above that the symmetrical methylene stretching bands disappear for alcohols, acids and alkyl bromides of the lower ratio of CH_2 to CH_3 groups whereas they appear for the hydrocarbons of the same ratio, may be understood as the shift of this band for three series of compounds towards the high frequency side, with the result of sufficient overlap with the methyl band at 2880 cm^{-1} region.

The inductive effect of the polar groups upon the methyl and the methylene groups in a molecule has been also found in the proton chemical shift of the nuclear magnetic resonance spectra¹⁹⁾ of methyl and ethyl derivatives of a number of organic substituent groups, though the resolution is not good enough for longer chain compounds.

C-H...Z Type Hydrogen Bond

Although considerable attention has been paid to the polarity of the C-H bond, in the present state the knowledge with respect to its sign seems to be somewhat

in confusion. In this paper, Pauling's theory^{12a)} of electronegativity has been adopted and C-H⁺ polarity is assumed. Since from equation 3 we have

$$x_{C_n} - x_{H_n} = (x_C^0 - x_H^0) + \alpha(1 - \sigma)\sigma^{n-1} > x_C^0 - x_H^0$$

it may be seen that the C-H bond is more polarized by the substitution of the electronegative group. In general, it is well known that the more Y-H⁺ bond is polarized the stronger the hydrogen bond Y-H...Z is²⁰⁾. Thus, the C-H...Z type hydrogen bond may be possibly formed between the C-H bond near the polar substituent and the electronegative group Z. This has been found infrared spectroscopically for some organic compounds in non aqueous solutions²¹⁾. Therefore, Palit's suggestion³⁾ concerning the possibility of hydrogen bond-formation between polarized C-H bond and water seems to be reasonable. However, its contribution to the solubility may be estimated very small on the basis of the fact that the solubility of alkyl bromide is extremely low in spite of their considerable inductive effect of the bromine atom on the methyl group as shown in Fig. 1.

Effect of Branching

While it has been shown that the numerical values of constants *A* and *B* for straight-chain compounds are in fairly good agreement with the theoretical results, the empirical values for branched-chain alcohol considerably differ from the theoretical ones for straight-chain alcohol (especially on *B* values). It may be attributed to the change in the charge ratio, σ , caused by the branching of carbon chain. If 0.40 is taken for σ value instead of 0.45, calculated values of constants *A* and *B* sufficiently agree with the empirical results for branched-chain alcohol as shown in the last row of Table 6. Thus, it may be suggested that the charge ratio decreases on branching of carbon chain.

Anomaly of CH₃X Type Molecule

As is shown in Fig.1 as well as in Tables 1, 2 and 3, the frequencies of the lowest members of homologous series examined show departure from the values expected by equation 1. Especially, the deviation of methyl bromide is remarkable. These facts suggest that the methyl groups in these molecules may be affected by some short range effects as well as the inductive effect discussed above. Therefore, further studies on the character of the methyl groups in CH₃X molecules are needed.

Electron-Withdrawing Power of Polar Group and Induced Charge of Carbon Chain

In the theoretical consideration, it has been assumed that both the electron-withdrawing power of the polar group and the induced charge on C₁ atom are independent of the carbon chain length. If the charge on C₁ atom varies with the chain length, it should decrease with the increase of the chain length on the basis of the electrical neutrality of the whole molecule, assuming that the electron-withdrawing power of the polar group is constant. On the other hand, from the fact that the electron-donating power of alkyl group increase with the increase of its chain length,²²⁾ it seems that the electron-withdrawing power of the polar group increase with the chain length as suggested by Ingold.^{23a)} Accordingly it is con-

ceivable that two factors mentioned above may change oppositely with each other with the change of the carbon chain length. Thus the assumption that two factors are independent of the chain length may be valid in first approximation.

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